

AD-753 105

COMPOSITION AND COMBUSTION CHARACTERIS-  
TICS OF CONDENSED EXHAUST FROM BORON-  
CONTAINING FUEL-RICH ROCKET MOTORS

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Atlantic Research

Prepared for:

Air Force Office of Scientific Research

October 1972

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AD-753 105

## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate authority) ATLANTIC RESEARCH CORPORATION SHIRLEY HIGHWAY AT EDSALL ROAD ALEXANDRIA, VIRGINIA 22314		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
3. REPORT TITLE COMPOSITION AND COMBUSTION CHARACTERISTICS OF CONDENSED EXHAUST FROM BORON-CONTAINING FUEL-RICH ROCKET MOTORS		2b. GROUP	
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Scientific Interim			
5. AUTHOR(S) (First name, middle initial, last name) ANDREJ MACEK J MCKENZIE SEMPLE			
6. REPORT DATE Oct 1972	7a. TOTAL NO. OF PAGES 9	7b. NO. OF REFS 4	
8a. CONTRACT OR GRANT NO. F44620-71-C-0124		9a. ORIGINAL REPORT NUMBER(S)	
b. PROJECT NO. 9711-01			
c. 61102F	9b. OTHER REPORT NO.(S) (Any other numbers that may be assigned this report) AFOSR - TR - 72 - 2379		
d. 681308			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited			
11. SUPPLEMENTARY NOTES TECH, OTHER		12. SPONSORING MILITARY ACTIVITY AF Office of Scientific Research (NAE) 1400 Wilson Blvd Arlington, Va. 22209	

13. ABSTRACT

The objective of this work has been to characterize the nature of the primary exhaust from fuel-rich boron-containing (ca. 50%) rocket motors, and to study its combustion. Two formulations were studied, each at two pressures. Solid materials collected from motor firings were examined microscopically, analyzed chemically, and studied for ignition temperatures and burning times,  $t_b$ . Both the theory and the experiment show that boron undergoes substantial chemical reaction in primary combustion. Both soluble and insoluble boron compounds form ( $B_2O_3$ ,  $Al_2MgO_4$ ,  $B_4C$  and others). The minimum gas temperatures for ignition of the exhaust material are the same as those for pure boron: 1980°K for fine particles (-10  $\mu m$ ) and 1850°K for 30-40  $\mu m$  particles. Burning times of the exhaust material are also roughly the same as for pure boron. Even through our measurement of  $t_b$  is rough, it appears that for small particles  $t_b$  is not proportional to  $d^2$ , but to a power of diameter closer to unity.

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NOV 63

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### KEY WORDS

**LINK A**

**LINK B**

LINK C

**ROLE**

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## PARTICLE COMBUSTION

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COMPOSITION AND COMBUSTION CHARACTERISTICS OF CONDENSED EXHAUST  
FROM BORON-CONTAINING FUEL-RICH ROCKET MOTORS\*

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INTRODUCTION

The thermodynamic attractiveness of boron for air-breathing propulsion purposes is well known. Two applications have aroused much interest recently: ducted air-breathing propulsion and external burning propulsion. The basic concept is the same in both cases: the exhaust material from an extremely fuel-rich primary motor burns in secondary air to yield high thrust. For best results the primary propellant must contain very large amounts, typically about 50% of boron. Consequently, the conditions in the primary motor are ill suited for combustion of boron. Primary temperatures are low and oxidants in such short supply that only a small fraction of boron can burn, even if it does ignite. Indeed, it is known that efficiency problems arise in ducted systems, and they must therefore be expected also in external-burning propulsion.

Substantial prior work has been reported on ignition and combustion of pure boron (References 1, 2 and 3). However, there remained a large uncertainty as to the nature (physical state, chemical composition) and especially as to combustion characteristics of the condensed material discharged from the primary motor, which is certainly not pure boron. The primary reaction must be expected to coat the existing particles with reaction products and/or to generate new particles. Agglomeration of particles is a definite possibility.

The objective of the present work has been to characterize the nature of the primary exhaust from fuel-rich motors, and to study its ignition and combustion characteristics, especially as compared to the known information for pure boron.

EXPERIMENTAL

Two primary propellants were studied. The first (ARCADENE 256A) was a CTPB formulation, and the second (ARCADENE 280) a polyester formulation. Each had roughly 50% of boron.

Four motors were prepared and fired, two with each formulation, into a closed tank containing about 7 psia of dry argon. The CTPB motors were fired at 30 and 590 psia (measured), and the polyester motors at 150 and 960 psia, respectively.

Samples of collected materials were (a) examined microscopically; (b) separated into soluble and insoluble portions and analyzed chemically for total boron in each portion; and (c) studied for ignition temperatures and burning times. The chemical analysis was performed by Ledoux Corporation.

\*Supported by Air Force Office of Scientific Research under Contract F44620-71-C-0124.

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Ignition and combustion studies were made by injecting solid particles into flame products of a gas burner. The gas-burner technique had been used very successfully in the past for detailed fundamental combustion studies of relatively large single particles. We have now developed a modification of that method, allowing quantitative ignition and combustion studies of streams of small particles ( $d < 10\mu$ ). This apparatus is shown in Figure 1. The main modification aspect was the addition of a second (lower) flotation chamber designed to break up particle clusters. The chamber is lightly packed with small plastic spheres which are set in motion by a high-velocity carrier-gas jet. A steady stream of particles can thus be introduced into burner gases for prolonged periods of time.

## RESULTS

Thermodynamic equilibrium computations have been made for chamber and exhaust conditions for the four measured pressures. The results are given Table 1. For the purpose of comparison of the experimental data with theory, we have assumed that the collected material consists of species which are solid, liquid, or condensable gases under exhaust conditions. The condensable gases contribute 10-12 weight percent.

Two sets of computations were made for each experimental run. The first set included  $B_4C$  and BN among the products; the second did not. The numerical results are given in Tables 2 and 3, along with the experimental results of the chemical analyses. Inspection of these tables shows that the theoretical calculations, while certainly not accurate, are quite indicative of the actual chemical composition. Since much of boron in the condensables appears in the three insoluble species-- $B$ ,  $B_4C$ , and BN--the experimental separation into soluble and insoluble portions does not suffice to decide which of the two sets of computations is more realistic.

Suspension of the collected material in various inert liquids showed that it had a rather wide density spectrum, 1.9 to 2.2 gm/cc. The original boron density was about 2.3 gm/cc. After washing of the collected material in hot alcohol, the density of the residue was somewhat above 2.3 gm/cc. This indicates that the relatively low-density material (e.g.  $B_2O_3$ ) coats, or is otherwise attached to, particles of higher density ( $B$ ,  $B_4C$ ).

Microscopic examination of the collected samples showed that they were loosely agglomerated into very large clusters, most of which could be broken up by ball-milling and sieving. Average diameters of the sieved material were 3-4 $\mu$ m. Some firm agglomerates,  $d > 20\mu$ m, persisted. Figure 2 shows micrographs of the material as collected and after sieving. Combustion of large agglomerates,  $30\mu < d < 40\mu$ m, was studied by previously developed single-particle techniques, and combustion of the fine material by the new experimental technique described earlier in this paper.

Minimum gas temperatures needed for ignition were measured both for single agglomerates and for continuous streams of small particles. This was done by observing the ignition (or failure to ignite) in a series of experiments in which gas temperatures were varied, while the mole fraction of oxygen, X, was kept constant at  $0.20 \pm 0.02$ . The minimum temperatures were found to be 1850°K for 30-40 $\mu$ m agglomerates and 1980°K for the fine

material. Both results agree very closely with the data obtained with pure boron: single crystals (Reference 1), and a sample of 98% amorphous boron with particle diameters about  $1\mu\text{m}$ .

Burning times ( $t_b$ ) of the collected material were also measured by both gas-burner techniques. 30-40 $\mu\text{m}$  agglomerates have roughly the same  $t_b$  values as the 35 $\mu\text{m}$  crystalline boron (Reference 3). Results of  $t_b$  in burner gases are given in Figure 3. The notation EM 101 and EM 104 refers to the collected material from two of the four motor firings. While the single-particle point is quite accurate, the  $t_b$  and the  $d$  values for all the other (fine) materials are very rough, perhaps no better than within a factor of 2. Nevertheless, it is evident that burning times are proportional to a power of the particle diameter much less than  $n=2$ , perhaps close to  $n=1$ .

### CONCLUSIONS

Both the thermodynamic computations of the primary combustion products and the experimental chemical analysis show that boron undergoes substantial chemical reaction in primary combustion. Furthermore, the quantitative analytical results are roughly consistent with the assumption of thermodynamic equilibrium; however, more detailed analytical data would be needed for a detailed comparison.

Perhaps the most direct result of this work is the finding that both the ignition temperatures and the subsequent burning times of the condensed primary exhaust are virtually the same as for pure boron. For the case of burning times,  $t_b$ , this is not very surprising, because one should expect particle combustion to be controlled by gas-phase rare processes, hence determined by gas properties and the particle diameter. It is more surprising for the case of ignition temperatures which one would expect to be affected by surface coatings. Even in this case, however, there is some confirmation from theory. King (Reference 4) in his theoretical study of boron particle ignition, which includes time-dependent processes of oxide-layer growth and vaporization, found that the effect of the initial layer thickness on ignition of particles is small.

Even though our measurement of  $t_b$  is rough, it appears clear that for small particles  $t_b$  is not proportional to  $d^2$ . Thus it is possible that the transition from the diffusion-limited to the kinetically limited regime takes place at diameter values not much below 30 $\mu\text{m}$ .

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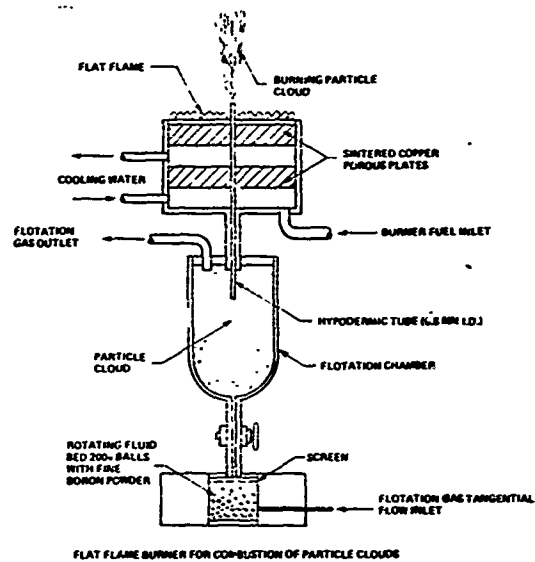
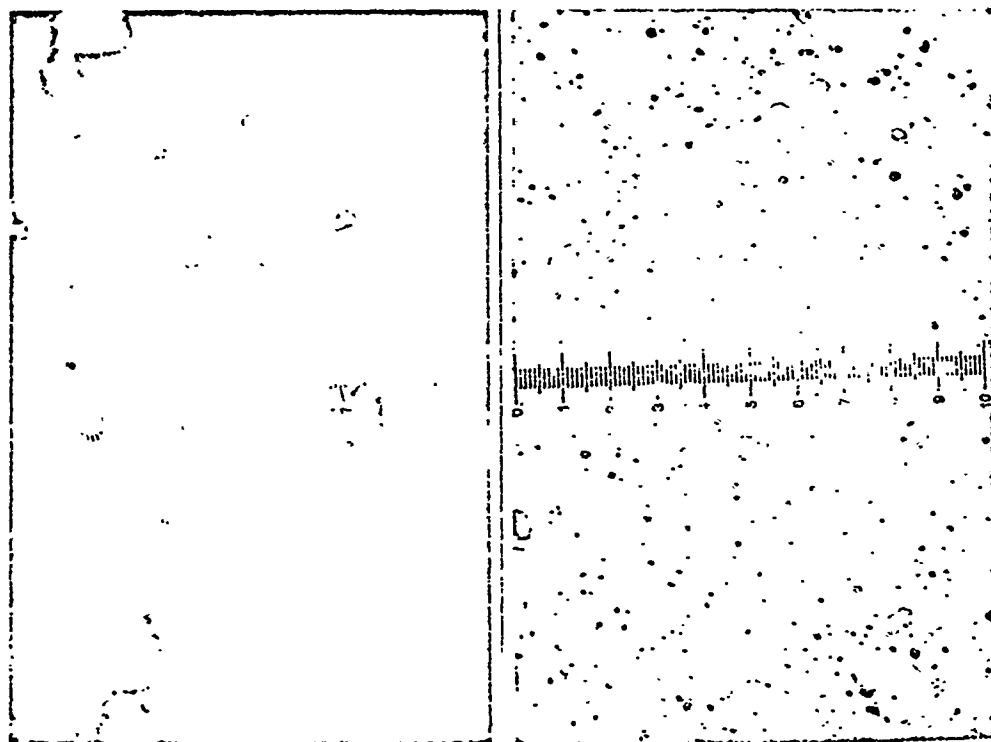


Figure 1. Flat-Flame Gas Burner for Combustion of Particle Clouds



SAMPLE 104    a. AS COLLECTED ( $5\mu$  PER SINGLE DIVISION)  
                  b. AFTER BALL-MILLING AND SIEVING ( $2.6\mu$  PER DIVISION)

Fig. 2 Micrographs of Samples Collected in  
Motor Test 104



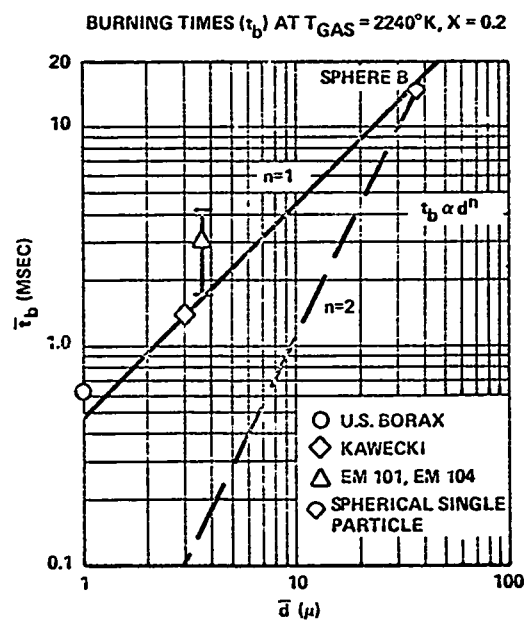


Figure 3. Burning Times ( $t_b$ ) of Various Particles

# THERMODYNAMIC CALCULATIONS

PROPELLANT	CHAMBER PRESSURE (psia)	CHAMBER TEMPERATURE (°K)	EXHAUST TEMPERATURE (°K)	PERCENT CONDENSABLE <sup>a</sup> (in exhaust)
256A	30	1,888	1,740	84.9
256A	590	2,071	1,618	88.9
280	150	2,136	1,872	83.7
280	960	2,409	1,858	86.6

<sup>a</sup>SOLIDS:  $B_4C$ , BN, B,  $MgAl_2O_4$ ,  $MgO$ , C

LIQUIDS:  $B_2O_3$ , Fe

GASES:  $MgCl_2$ ,  $B_2O_2$ ,  $B_2O_3$ , Mg, HCl,  $B_3H_3O_3$ ,  $HBO_2$ , BOCI, BO,  $AlBO_2$ , AlCl,  $FeCl_2$

Table 1. Thermodynamic Equilibrium Calculations

RUN NUMBER	101	102	103	104
PROPELLANT	280	256A	280	256A
CHAMBER PRESSURE (PSIA)	150	30	960	590
INSOLUBLE PERCENT OF CONDENSABLES				
(a) COMPUTED WITH $B_4C$ , BN	70.0	80.0	68.5	77.5
(b) COMPUTED WITHOUT $B_4C$ , BN	71.0	75.5	68.3	72.3
(c) EXPERIMENTAL	73.1	84.8	74.5	58.4
PERCENT BORON IN CONDENSABLES				
(a) COMPUTED WITH $B_4C$ , BN	51.6	52.7	50.6	50.2
(b) COMPUTED WITHOUT $B_4C$ , BN	56.4	47.4	49.5	44.8
(c) EXPERIMENTAL	46.6	58.5	44.3	35.6

Table 2. Condensable Exhaust: Computation and Experiment

RUN NUMBER	101	102	103	104
PROPELLANT	280	256A	280	256A
CHAMBER PRESSURE (PSIA)	150	30	960	590
PERCENT BORON IN INSOLUBLES				
(a) COMPUTED WITH $B_4C$ , BN	64.1	62.5	62.3	60.3
(b) COMPUTED WITHOUT $B_4C$ , BN	70.5	62.5	67.9	59.8
(c) EXPERIMENTAL	57.3	64.2	51.0	55.4
PERCENT BORON IN SOLUBLES				
(a) COMPUTED WITH $B_4C$ , BN	22.6	13.9	25.0	15.9
(b) COMPUTED WITHOUT $B_4C$ , BN	21.7	17.0	22.7	19.0
(c) EXPERIMENTAL	17.8	27.0	24.7	8.6

Table 3. Distribution of Boron in the Condensable Exhaust:  
Computation and Experiment